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(54) **Water-reducing admixtures for cementitious compositions**

Wasserreduzierende Gemische für Zementzusammensetzungen

Mélanges réducteurs d'eau pour compositions de ciment

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(73) Proprietors:
- **SANDOZ LTD.**
  4002 Basel (CH)
  Designated Contracting States:
  CH FR GB IT LI
- **SANDOZ-PATENT-GMBH**
  79539 Lörrach (DE)
  Designated Contracting States:
  DE

(72) Inventors:
- **Minomiya, Yoshikazu**
  Odawara-shi, Kanagawa (JP)
- **Ohta, Akira**
  Chigasaki-shi, Kanagawa (JP)
- **Yaguchi, Minoru**
  Fujisawa-shi, Kanagawa (JP)

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- **DATABASE WPI Section Ch, Week 8506, Derwent Publications Ltd., London, GB; Class D16, AN 85-034254 & JP-A-59 227 753 (NISSO MASTER BUILDERS)**
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Description

This invention relates to an admixture for cementitious compositions such as grouts, mortars and concretes.

Increasing difficulty in and expense of obtaining high quality aggregate for use in cementitious compositions such as concrete has forced manufacturers to resort to lower grade materials such as crushed stone, marine sand and even crushed concrete obtained from the demolition of old structures. This leads to problems with the concrete such as higher water demand, bleeding and lower workability and pumpability. It has been attempted to overcome these problems by means of admixtures. Typical of such admixtures are those already well known in the art, such as lignosulphonates, naphthalene sulphonate-formaldehyde condensates and various saccharides. Such materials reduce water requirement but also delay setting of the concrete, something which is not always desirable.

It has now been found that a blend of particular materials can greatly decrease the quantity of water required for a given cementitious mix while not significantly increasing set time. In addition, the blend does not cause excessive aeration (a major problem with some known admixtures) and it inhibits bleeding and improves workability. The invention therefore provides an admixture for use in a cementitious composition, which admixture consists of

(a) from 75-25% by weight of a water-reducing agent whose major component is a polycarboxylate; and

(b) from 25-75% by weight of at least one saccharide component selected from hydrogenated saccharides and polyhydric alcohol adducts of saccharides.

The water-reducing agent has as a major component a polycarboxylate which is known to be a water-reducing agent in its own right. By "major component" is meant that the polycarboxylate or polycarboxylates (it is permissible to use more than one such material) is present in higher weight proportion than any other individual component in the water-reducing agent. It is therefore possible for the polycarboxylate to comprise less than 50% of the weight of the water-reducing agent, although it is preferable that it comprises at least 50%. More preferably, the water reducing agent comprises at least 60% by weight of polycarboxylate and most preferably it is 100% polycarboxylate. Typical examples include poly(acrylate salt-acrylate ester) copolymers, poly(methacrylic acid-methacrylate) copolymers, poly(styrene-maleate salt) copolymers, and poly(styrene-maleate ester) copolymers. Such materials are readily available commercially, for example, the SP-8 series of materials from NMB Ltd.

The water-reducing agent may additionally contain at least one other noncarboxylate water-reducing agent. Any known water-reducing agent is satisfactory and typical examples include lignosulphonates and naphthalene sulphonate-formaldehyde condensates.

The hydrogenated saccharides which are one possibility for use in this invention as a saccharide component as hereinabove mentioned may be derived from mono- or disaccharides, but are preferably derived from polysaccharides, more preferably starches. Examples of suitable saccharides which may be hydrogenated include starch hydrolysates, glucose fermentation products, celluloses, cellulose hydrolysates, hemicelluloses and hemicellulose hydrolystes, starch hydrolysates being especially desirable. Commercial examples of suitable materials include D-Sorbit and PO-20 of Towa Kasei and SE-100 of Nikken Kagaku. Other materials include hydrogenated oligosaccharides, for example, of the type described in United States Patent 4,073,658.

The polyhydric alcohol adducts of saccharides which are the other possibility for use as a saccharide component are materials wherein the saccharide has an average molecular weight of from 2,000 - 10,000. and they additionally comprise polyhydric alcohol residues added at the end of the saccharide chains. The preferred polyhydric alcohols are alkylene and polyalkylene glycols, glycerol, xylitol, erythritol and sorbitol, most preferred being polyethylene glycol or polypropylene glycol present such that the number of mols of ethylene oxide or propylene oxide present per mol of saccharide is from 1 - 100 - larger polyethylene and polypropylene glycols (especially the former) give rise to higher air-entraining properties, which is usually not desirable.

When hydrogenated saccharides are used as the saccharide component, they are preferably present as a mixture of which

(i) 70-30% by weight (on total weight of hydrogenated saccharides) have molecular weights in the range 180-300;
(ii) 30-70% by weight have molecular weight of from 300 up to 4.000: and
(iii) 30% by weight maximum have molecular weights of 4.000 and over.

These proportions may have a considerable effect on the invention. For example. a proportion of greater than 30% of material of molecular weight 4.000 and above results in a lowered workability and greater water demand. This also occurs when the proportion of the other molecular weight materials falls outside the stated proportions. The excellent properties of the invention are not fully realized in this case when only one or the other of the two hydrogenated saccharides (i) and (ii) is used - the presence of both gives best results.

The dosage of the admixture of this invention is dependent on the cement composition used, but basically it will suffice for it to be in sufficient quantity to impart the desired water reduction and adequate workability to the composition. A typical quantity is 0.05 to 3.00 percent of the admixture by weight of cement.

It is possible and permissible to use other admixtures in conjunction with the admixture of this invention to achieve particular results.Typical examples of suitable admixtures include air-entraining agents, shrinkage reducing agents, accelerating agents, retarding agents, foaming agents, defoaming agents, rust-inhibiting agents, quick-setting agents and water-soluble polymer substances.

The admixture of this invention may be used in generally-used cement compositions such as cement. paste, mortar, grout, and concrete as a matter of course, but it is especially useful in the manufacture of cementitious compositions of comparatively high unit water contents due to the influence of the aggregate used, cementitious compositions for which good workability cannot be obtained by other means. lean-mix concrete of low unit cement content with which good workability is difficult to obtain, pumped concrete, high-strength concrete. cement products, masonry mortar and injection grout.

The invention therefore also provides a method of reducing the water demand of a cementitious composition by the addition thereto of an admixture as hereinabove defined. The components may be added individually to the composition, but it is preferred to add them simultaneously, and more preferably as a blend.

The invention additionally provides an cementitious composition which comprises an admixture as hereinabove defined.

The invention is further described with references to the following non-limiting examples in which all parts are expressed by weight.

Manufacturing Example 1

Four hundred parts of starch hydroysate and 20 parts of xylitol are added to 100 parts of anhydrous toluene and the mixture heated to 80°C, at which point 10 parts of tungstophosphoric acid is added and stirring is carried out for 30 minutes. Reaction is then stopped by adding distilled water. The mixture is neutralised and the solvent is removed. The mixture is purified, and all matter of molecular weight exceeding 10,000 is removed by ultrafiltration. The resulting product is designated Sample A.

Manufacturing Example 2

Four hundred parts of starch hydrolysate and 20 parts of erythritol are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample B is obtained.

Manufacturing Example 3

Four hundred parts of starch hydrolysates and 20 parts of sorbitol are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample C is obtained.

Manufacturing Example 4

Four hundred parts of starch hydrolysates and 20 parts of glycerol are added to 100 parts of anhydrous toluene. and the procedures of Manufacturing Example 1 are carried out. Sample D is obtained.

Manufacturing Example 5

Four hundred parts of starch hydrolysate and 5 parts of ethylene glycol (1 mol) are added to 100 parts of anhydrous toluene. and the procedures of Manufacturing Example 1 are carried out. Sample E is obtained.

Manufacturing Example 6

One hundred parts of starch hydrolysate and 20 parts of ethylene glycol (4 mols) are added to 100 parts of anhydrous toluene. and the procedures of Manufacturing Example 1 are carried out. Sample F is obtained.

Manufacturing Example 7

One hundred parts of starch hydrolysate and 60 parts of ethylene glycol (12 mols) are added to 100 parts of anhydrous toluene. and the procedures of Manufacturing Example 1 are carried out. Sample G is obtained.

Manufacturing Example 8

One hundred parts of starch hydrolysate and 120 parts of ehtylene glycol (24 mols) are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample H is obtained.

Manufacturing Example 9

One hundred parts of starch hydrolysate and 250 parts of ethylene glycol (50 mols) are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample I is obtained.

Manufacturing Example 10

One hundred parts of starch hydrolysate and 500 parts of ethylene glycol (100 mols) are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample J is obtained.

Manufacturing Example 11

One hundred parts of starch hydrolysate and 10 parts of propylene glycol (1 mol) are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample K is obtained.

Manufacturing Example 12

One hundred parts of starch hydrolysate and 40 parts of propylene glycol (4 mols) are added to 100 parts of anhydrous toluene, and the procedures of Manufacturing Example 1 are carried out. Sample L is obtained.

Mortar and Concrete Examples

1) Mix Proportions, Preparation and Materials of Mortar and Concrete

1-1) Mortar

Mortar is designed for flow of 200 to 210 mm and target air content of 8.0 volume percent in accordance with the mix proportions of Table 1, and prepared with the respective materials measured for a yield as mixed of 5 litres. with mixing done for 120 seconds after introduction of all materials into an ASTM mortar mixer.

1-2) Concrete

Concrete is designed for target slump of 18.0 ± 0.5 cm and target air content of 4.5 ± 0.5 volume percent in accordance with the mix proportions of Table 2. and prepared with the respective materials measured out for a yield as mixed of 80 liters, with mixing done for 90 seconds after introduction of all materials into a 100-liter pan-type power-driven blade mixer.

1-3) Materials

a) Fine aggregate:
Oi River system pit sand (specific gravity = 2.58. fineness modulus = 2.76):

b) Coarse aggregate:
Ohme graywacke crushed stone (specific gravity = 2.65, maximum size = 20 mm):

c) Cement:
Ordinary portland cement (specific gravity = 3.16. mixture in equal parts of cement manufactured by Onoda. Sumitomo. and Mitsubishi firms):

d) Water-reducing agent:
A polycarboxylate which is a copolymer of methacrylate salt and methacrylate ester (abbreviated as PCA in Table 3 and Table 4)
Lignosulphonate (abbreviated as Lig in Table 3 and Table 4)
Melamine sulphonate-formalin condensate (abbreviated as MS in Table 3 and Table 4)
Naphthalene sulphonate-formalin condensate (abbreviated as BNS in Table 3 and Table 4):

A carboxylate which is a copolymer and maleate (abbreviated as SMA in Table 3 and 4)

e) Hydrogenated saccharide:
Hydrogenated hydrolysed starches, such as D-Sorbit and PO-20 manufactured by Towa Kasei Kogyo, and Sorbit C, SE-100 manufactured by Nikken Kagaku, designated bl, b2, and b3, obtained by fractioning to the molecular weights of 180-<300, >300 and >4.000 respectively by an ultrafiltration apparatus (a Lab Module Type 20 ex DDS Corp. Denmark).
Polyhydric alcohol adduct of saccharides

Sample A: (Average molecular weight = 3,000)
Sample B: (Average molecular weight = 3,100)
Sample C: (Average molecular weight = 3,100)
Sample D: (Average molecular weight = 3,000)
Sample E: (Average molecular weight = 2,900)
Sample F: (Average molecular weight = 3,100)
Sample G: (Average molecular weight = 3,300)
Sample H: (Average molecular weight = 3,800)
Sample I: (Average molecular weight = 3,400)
Sample J: (Average molecular weight = 9,800)
Sample K: (Average molecular weight = 2,900)
Sample L: (Average molecular weight = 3,100)
Sample M: (Polyethlene glycol adduct of 30-80, mfd, by Towa Kasei, average molecular weight = 3,200)
Sample N: (Glycerol adduct of starch hydrolysate, mfd. by Towa Kasei, average molecular weight = 350)
Sample O: (Propylene glycol adduct of starch hydrolysate, mfd. by Towa Kasei, average molecular weight = 250)
Sample P: Polyethylene glycol adduct of starch hydrolysate, average molecular weight = 13,000, ethylene glycol 24-mol adduct)
Sample Q: (Polyethylene glycol adduct of starch hydrolysate, average molecular weight = 5,100, ethylene glycol 120-mol adduct)

2) Methods of testing Mortar and Concrete

2-1) Mortar
Water-reducing properties and air-entraining properties of mortar are evaluated measuring flow and air content.

a) Flow:
In accordance with JIS A 5201:
b) Air content:
In accordance with JIS A 1116:
c) Water-reducing property evaluation:
Water-reducing property is evaluated by the difference between flow when using the additive and flow of plain mortar:
d) Existence of synergistic improvement in water-reducing property:
It is indicated whether the increase in water-reducing property of the water-reducing agent is synergistically improved or is an aggregate sum.

The test results are given in Tables 3 and 4.

2-2) Concrete
Concrete is evaluated by time of setting, bleeding, and visual observation of workability in accordance with the following criteria. Compressive strength at 28-day stage is also measured (see Table 5).

a) Slump:
In accordance with JIS A 1101:

b) Air content:
In accordance with JIS A 1128.

c) Compressive strength:
In accordance with JIS A 1118 and JIS A 1132.

d) Time of setting:
In accordance with Appendix 2, JIS A 6204.

e) Bleeding:
In accordance with JIS A 1123.

f) Visual observation:
Workability was evaluated by visual observation as described below.

A (good): The concrete flows smoothly, without any segregation of the aggregate being seen.

B (ordinary): Smooth flow, but with a degree of "crumbling" (evident presence of coarse aggregate).

C (poor): Much coarse aggregate clearly visible poor flow or no flow at all.

3) Test Results

3-1) Mortar

The results of tests with mortar are given in Tables 3 (hydrogenated saccharide) and 4 (polyhydric alcohol adduct of saccharide). In Table 3, the test results of Examples 1 to 13, and the results of plain mortar completely free of water-reducing agents or other cement additives (Comparison Example 1), and mortars with addition of only water-reducing agent (Comparison Example 2), only hydrogenated saccharides (Comparison Examples 3 to 6), and hydrogenated saccharides mixed with water-reducing agent (Comparison Examples 7 to 13) are given.

As can be seen in the results given in Table 3, when the cement additive of this invention is used in mortar (Examples 1 to 12), the following observations may be made:

a) Water-reducing Properties

Comparison Example 1 is a case of plain mortar in which there is completely no addition of admixture and the increase in water-reducing properties is evaluated with the flow value of this mortar as the basis.

Examples 1 to 5 are cases of the proportions of b1 and b2 being varied. It can be seen that, when bl is in the range of 70 to 30 weight percent and b2 30 to 70 weight percent, the water-reducing properties of the admixture exceeds the aggregated individual water-reducing properties of the water-reducing agent, indicating a synergistic effect and a considerable and unexpected increase in water-reducing properties. In contrast. Comparison Examples 10 and 11 are cases where the mixture ratios of b1 and b2 lie outside the abovementioned ranges of b1 and b2. In these cases. the water-reducing properties of a combination of such materials is merely the aggregate of the water-reducing properties of the individual components.

Examples 6 to 8 are cases wherein the proportion of b3 is varied. It can be seen that. when the quantity of b3 present is not more than 30 weight percent of the total quantity of hydrogenated saccharide, there is no coagulation, and the same synergistic water-reducing properties reported hereinabove are again observed. In contrast. Comparison Example 9 and Comparison Example 12 are cases where the proportions of b3 exceeding 30 weight percent of the total quantity of hydrogenated saccharides and in these cases mortar will coagulate. In the case of Comparison Example 5 where b3 alone is used. coagulation is considerable.

Examples 9 and 10 are cases wherein the mixture proportions of water-reducing agent and hydrogenated saccharides are varied. When the ranges of 75 to 25 weight percent water-reducing agent and 25 to 75 weight percent hydrogenated saccharides are used. the water-reducing properties of the combination exceeds the aggregate of the individual water-reducing properties of the water-reducing agent and the hydrogenated saccharides: the effect is synergistic. with considerable improvements in water-reducing properties. In contrast. Comparison Examples 13 and 14 are cases where the ranges of water-reducing agent and hydrogenated saccharides lie outside those given hereinabove. In these cases. the water-reducing properties of combination of the water-reducing agent and the hydrogenated saccharides are the aggregate of the individual water-reducing properties.

Examples 11 to 13 are cases of lignosulfonate (Lig). melamine sulfonate-formalin condensate (MS), and naphthalene sulfonate-formalin condensate (BNS) combined as other ingredients with polycarboxy-

late (PCA) as the water-reducing agent. When these other water-reducing agents are combined with polycarboxylate, provided that the ratio of the polycarboxylate water-reducing agent and the hydrogenated polysaccharide is kept within the limits of this invention, the synergistic effect previously reported is still given.

In Comparison Example 6, b1 and b2 are combined at a ratio of 1:1, and in this case, the aggregate water-reducing properties of this combination is the aggregate of the individual water-reducing properties of b1 and b2. Comparison Examples 7 and 8 are respectively examples of a water-reducing agent combined with b1 or b2 alone, and in such cases only the aggregate of the water-reducing properties of the individual components is given.

b) Air entraining Properties
On comparing air contents in Examples 1 to 13, they are approximately of the same degree as in Comparison Example 2, and air is not excessively entrained.

Table 4 similarly shows the advantages of using polyhydric alcohol adducts of saccharides.

3-2) Concrete

The results of tests with concrete are given in Table 5. The concretes listed in Table 5 are all prepared such that they have slumps in the range 18.0 ± 0.5 cm and air contents of 4.5 ± 0.5%. In Table 5, the results of tests performed on Examples 33-38 (hydrogenated saccharide-containing) and 39-45 (polyhydric alcohol adduct of saccharide-containing) and on concretes utilising water-reducing agents not combined with hydrogenated saccharides (Comparison Examples 21 to 24) comparing setting times, compressive strengths, bleeding, and workability are indicated.
As seen in the results given in Table 5, on examination of the cases wherein the admixture of this invention is used in concrete (Examples 33-45), the following effects are observed:

a) Water-reducing Properties
As is clear from comparing Examples 33 and 34 with Comparison Example 21, and Examples 35-38 with Comparison Examples 22-24, approximately the same slumps are obtained in the examples even when the dosages of admixtures are smaller than in the Comparison Examples. and it can be seen that water-reducing properties have been improved.

b) Air-entraining properties
Air contents are found to be in the range of 4.5 ± 0.5% (without using a defoaming agent) and the air-entraining properties are low.

c) Bleeding
As is clear on comparing with the Comparison Examples, bleeding is considerably reduced and segregation is inhibited.

d) Workability (Visual Observation)
Comparison with the Comparison Examples shows that all examples exhibit good workability.

e) Setting Time
As is clear on comparing with Comparison Examples, setting time is about 20 to 30 minutes faster than when using a water-reducing agent alone. and there is little or no set retardation.

f) Compressive Strength (28-Day)
As is clear on comparing with the Comparison Examples, there are attained compressive strengths of about the same degree as those given when using water-reducing agent alone.

TABLE 1

Water-Cement Ratio	Sand-Cement Ratio	Unit Content (g)		
		Water	Cement	Fine Aggregate
0.45	2.75	450	1.000	2.750

TABLE 2

Water-Cement Ratio	Sand-Aggregate Ratio %	Unit Content (g)			
		Water	Cement	Aggregate	
				Fine	Coarse
0.60	46.0	185	285	807	973

Table 3

	water reducing agent	Kind	Dosage[1)]	Hydrogenated Saccharide Composition, wt % b1	b2	b3	Dosage[1)]	Flow (mm)	Air (%)	Flow Increase (mm)	Synergistric Effect in Water Reduction
Example	1	PCA	0.30	70	30	0	0.20	247	6.2	67	yes
	2	PCA	0.30	60	40	0	0.20	247	6.1	67	yes
	3	PCA	0.30	50	50	0	0.20	246	6.2	66	yes
	4	PCA	0.30	40	60	0	0.20	245	6.2	65	yes
	5	PCA	0.30	30	70	0	0.20	243	6.0	63	yes
	6	PCA	0.30	50	40	10	0.20	246	6.1	66	yes
	7	PCA	0.30	50	35	15	0.20	240	6.0	60	yes
	8	PCA	0.30	40	40	20	0.20	238	5.9	58	yes
	9	PCA	0.30	60	40	0	0.15	235	5.7	55	yes
	10	PCA	0.30	50	50	0	0.15	235	5.6	55	yes
	11	PCA Lig	0.25 0.05	60	40	0	0.20	247	6.3	67	yes
	12	PCA MS	0.25 0.05	60	40	0	0.20	248	6.0	68	yes

Table 3 (cont'd)

				b1	b2	b3					
	13	PCA BNS	0.25 0.05	60	40	0	0.20	248	6.1	68	yes
	14	SMA	0.30	60	40	0	0.20	248	6.1	68	yes
Compa-rison Example	1	-	-	-	-	-	-	180	3.1	-	-
	2	PCA	0.30	-	-	-	-	209	5.1	29	No
	3	-	-	100	-	-	0.20	194	5.3	14	No
	4	-	-	-	100	-	0.20	185	5.3	5	No
	5	-	-	-	-	100	0.20	108	5.4	-72	No
	6	-	-	50	50	-	0.20	189	5.4	9	No
	7	PCA	0.30	100	-	-	0.20	221	6.1	41	No
	8	PCA	0.30	-	100	-	0.20	211	6.1	31	No
	9	PCA	0.30	-	-	100	0.20	145	6.0	-35	No
	10	PCA	0.30	75	25	0	0.20	220	6.2	40	No
	11	PCA	0.30	25	75	0	0.20	216	6.1	36	No
	12	PCA	0.30	41	28	31	0.20	198	6.0	18	No
	13	PCA	0.30	60	40	0	0.10	214	5.9	34	No
	14	PCA	0.10	60	40	0	0.30	205	6.4	25	No

Note 1) Dosage of cement additive by weight percent to weight of cement (in terms of solids).

Table 4

		Water-reducing agent		Polyhydric Alcohol Adduct of Saccharide		Flow (mm)	Air (%)	Flow increase (mm)	Synergistic Effect in Water Reduction
		Kind	Dosage [1]	Kind	Dosage [1]				
Example	15	PCA	0.30	Sample A	0.20	250	6.1	70	Yes
	16	PCA	0.30	Sample B	0.20	250	5.9	70	Yes
	17	PCA	0.30	Sample C	0.20	251	6.2	71	Yes
	18	PCA	0.30	Sample D	0.20	250	6.0	70	Yes
	19	PCA	0.30	Sample E	0.20	251	6.1	71	Yes
	20	PCA	0.30	Sample F	0.20	248	6.2	69	Yes
	21	PCA	0.30	Sample G	0.20	250	6.0	70	Yes
	22	PCA	0.30	Sample H	0.20	252	6.1	72	Yes
	23	PCA	0.30	Sample I	0.20	248	6.5	68	Yes
	24	PCA	0.30	Sample J	0.20	250	7.0	70	Yes
	25	PCA	0.30	Sample K	0.20	251	6.0	71	Yes
	26	PCA	0.30	Sample L	0.20	253	6.1	73	Yes
	27	PCA	0.30	Sample M	0.20	254	5.9	74	Yes
	28	PCA	0.30	Sample N	0.20	253	6.0	73	Yes
	29	PCA	0.30	Sample O	0.20	253	6.0	73	Yes
	30	SMA	0.30	Sample P	0.20	253	6.0	73	Yes
	31	PCA BNS	0.25 0.05	Sample Q	0.20	253	6.0	73	Yes

Table 4 (cont'd)

	32	PCA MS	0.25 0.05	Sample G	0.20	253	6.0	73	Yes
Comparison Example	15	-	-	Sample A	0.20	193	5.4	13	No
	16	-	-	Sample D	0.28	183	5.8	13	No
	17	-	-	Sample C	0.20	193	5.4	15	No
	18	-	-	Sample G	0.20	199	5.5	19	No
	19	PCA	0.30	Sample P	0.20	160	6.0	-20	No
	20	PCA	0.30	Sample Q	0.30	243	13.5	63	Yes

Note 1) Dosage of cement additive by weight percent to weight of cement (in terms of solids).

Table 5

	water-reducing agent			Hydrogenated Saccharide Composition, wt %				Polyhydric Alcohol Adduct of Saccharide		Setting Time (hr-min)		Compressive Strength (28-Day) (kgf/cm^2)	Bleeding (cm^3 / cm^2)	Workability Evaluation
		Kind	Dosage[1]	b1	b2	b3	Dosage[1]	Kind	Dosage[1]	Initial	Final			
Example	33	PCA	0.15	60	40	0	0.10	-	-	6-10	8-10	327	0.25	A
	34	PCA	0.15	50	30	10	0.10	-	-	6-15	8-20	330	0.26	A
	35	PCA Lig	0.10 0.05	60	40	0	0.10	-	-	6-40	8-45	325	0.28	A
	36	PCA MS	0.10 0.05	60	40	0	0.10	-	-	6-00	8-00	328	0.26	A
	37	PCA BNS	0.10 0.05	60	40	0	0.10	-	-	6-20	8-20	326	0.27	A
	38	SMA	0.15	60	40	0	0.10	-	-	6-15	8-25	322	0.25	A
	39	PCA	0.15	-	-	-	-	Sample B	0.10	6-10	8-10	327	0.25	A
	40	PCA	0.15	-	-	-	-	Sample B	0.10	6-15	8-20	330	0.26	A
	41	PCA Lig	0.10 0.05	-	-	-	-	Sample B	0.10	6-35	8-40	326	0.26	A
	42	PCA MS	0.10 0.05	-	-	-	-	Sample B	0.10	6-05	8-05	329	0.24	A
	43	PCA BNS	0.10 0.05	-	-	-	-	Sample B	0.10	6-15	8-15	327	0.25	A

	44	SMA	0.15	-	-	-	-	Sample B	0.10	6-15	8-25	322	0.25	A
	45	PCA	0.15	60	30	10	0.05	Sample B	0.05	6-15	8-25	322	0.25	A
Com-parison Example	21	PCA	0.30	-	-	-	-	-	-	6-45	8-55	322	0.35	B
	22	PCA Lig	0.20 0.10	-	-	-	-	-	-	6-50	8-50	324	0.37	C
	23	PCA MS	0.20 0.10	-	-	-	-	-	-	6-30	8-30	322	0.35	C
	24	PCA BNS	0.20 0.10	-	-	-	-	-	-	6-40	8.35	322	0.34	B

Note 1) Dosage of cement additive by weight percent to weight of cement (in terms of solids)

Claims

1. An admixture for use in a cementitious composition, which admixture consists of

   (a) from 75-25% by weight of a water-reducing agent whose major component is a polycarboxylate; and

   (b) from 25-75% by weight of at least one saccharide component selected from hydrogenated saccharides and polyhydric alcohol adducts of saccharides.

2. An admixture according to claim 1, wherein the water reducing agent comprises at least 60% by weight, preferably 100% by weight, of polycarboxylate.

3. An admixture according to claim 1 or claim 2, wherein the polycarboxylate is selected from poly(acrylate salt-acrylate ester) copolymers, poly(methacrylic acid-methacrylate) copolymers, poly(styrene-maleate salt) copolymers. and poly(styrene-maleate ester) copolymers.

4. An admixture according to any one of the preceding claims, wherein the saccharide component comprises hydrogenated saccharide in which

   (i) 70-30% by weight (on total weight of hydrogenated saccharides) have molecular weights in the range 180-300;
   (ii) 30-70% by weight have molecular weight of from 300 up to 4,000: and
   (iii) 30% by weight maximum have molecular weights of 4,000 and over.

5. An admixture according to any one of claims 1-3, wherein the hydrogenated saccharide is a polysaccharide, preferably a hydrogenated hemicellulose or a hydrogenated hydrolysed starch.

6. An admixture according to any one of claims 1-3, wherein the polyhydric alcohol from which the polyhydric alcohol adduct of a polysaccharide is derived is selected from alkylene and polyalkylene glycols, glycerol, xylitol, erythritol and sorbitol; preferably from polyethylene glycol or polypropylene glycol present such that the number of mols of ethylene oxide or propylene oxide present per mol of saccharide is from 1 - 100.

7. A method of reducing the water demand of a cementitious composition by the addition thereto of an admixture according to any one of the previous claims.

8. A cementitious composition which comprises an admixture according to any one of claims 1-6.

Patentansprüche

1. Zusatzmittel zur Verwendung für eine zementartige Zusammensetzung, wobei das Zusatzmittel aus

   (a) 75 bis 25 Gew.-% eines wasserreduzierenden Mittels. dessen Hauptkomponente ein Polycarboxylat ist, und
   (b) 25 bis 75 Gew.-% mindestens einer Saccharidkomponente ausgewählt aus hydrierten Sacchariden und Addukten aus mehrwertigen Alkoholen und Sacchariden

   besteht.

2. Zusatzmittel nach Anspruch 1. worin das wasserreduzierende Mittel mindestens 60 Gew.-%, bevorzugt 100 Gew.-%. Polycarboxylat umfaßt.

3. Zusatzmittel nach Anspruch 1 oder Anspruch 2. worin das Carboxylat ausgewählt ist aus Poly(acrylatsalzacrylatester)-Copolymeren. Poly(methacrylsäure-methacrylat)-Copolymeren, Poly(styrol-maleatsalz)-Copolymeren und Poly(styrol-maleatester)-Copolymeren.

4. Zusatzmittel nach einem der vorhergehenden Ansprüche. wonn die Saccharidkomponente ein hydriertes Saccharid umfaßt. bei dem

(i) 70 bis 30 Gew.-% (bezogen auf das Gesamtgewicht der hydrierten Saccharide) ein Molekulargewicht im Bereich von 180 bis 300 haben:
(ii) 30 bis 70 Gew.-% ein Molekulargewicht von 300 bis zu 4.000 haben und
(iii) maximal 30 Gew.-% ein Molekulargewicht von 4.000 und darüber haben.

5. Zusatzmittel nach einem der Ansprüche 1 bis 3, worin das hydrierte Saccharid ein Polysaccharid ist, bevorzugt eine hydrierte Hemicellulose oder eine hydrierte hydrolysierte Stärke.

6. Zusatzmittel nach einem der Ansprüche 1 bis 3, worin der mehrwertige Alkohol, von dem das Addukt aus mehrwertigem Alkohol und Polysaccharid abgeleitet ist, ausgewählt ist aus Alkylen- und Polyalkylenglykolen, Glycerin, Xylit, Erythrit und Sorbit. bevorzugt aus Polyethylenglykol oder Polypropylenglykol, die in einem solchen Anteil vorhanden sind, daß die Anzahl Mol Ethylenoxid oder Propylenoxid pro Mol Saccharid 1 bis 100 ist.

7. Verfahren zur Reduktion des Wasserbedarfs einer zementartigen Zusammensetzung durch Zugabe eines Zusatzmittels nach einem der vorhergehenden Ansprüche.

8. Zementartige Zusammensetzung enthaltend ein Zusatzmittel nach einem der Ansprüche 1 bis 6.

Revendications

1. Un adjuvant pour une utilisation dans une composition à base de ciment, ledit adjuvant comprenant

(a) de 75 à 25% en poids d'un agent réducteur d'eau dont le composant principal est un polycarboxylate, et
(b) de 25 à 75% en poids d'au moins un composant à base de saccharide choisi parmi les saccharides hydrogénés et les produits d'addition d'un alcool polyhydrique sur des saccharides.

2. Un adjuvant selon la revendication 1, dans lequel l'agent réducteur d'eau comprend au moins 60% en poids, de préférence 100% en poids de polycarboxylate.

3. Un adjuvant selon la revendication 1 ou 2, dans lequel le polycarboxylate est choisi parmi les copolymères de sel acrylate et d'ester acrylique, les copolymères de l'acide méthacrylique et du méthacrylate, les copolymères du styrène et du sel maléate et les copolymères du styrène et de l'ester maléique.

4. Un adjuvant selon l'une quelconque des revendications précédentes, dans lequel le composant à base de saccharide comprend un saccharide hydrogéné dans lequel

(i) de 70 à 30% en poids (par rapport au poids total des saccharides hydrogénés) ont des poids moléculaires compris entre 180 et 300:
(ii) de 30 à 70% en poids ont un poids moléculaire compris entre 300 et jusqu'à 4000: et
(iii) 30% en poids au maximum ont des poids moléculaires de 4000 et plus.

5. Un adjuvant selon l'une quelconque des revendications 1 à 3. dans lequel le saccharide hydrogéné est un polysaccharide, de préférence de l'hémicellulose hydrogénée ou de l'amidon hydrolysé hydrogéné.

6. Un adjuvant selon l'une quelconque des revendications 1 à 3, dans lequel l'alcool polyhydrique dont est dérivé le produit d'addition de l'alcool polyhydrique sur un polysaccharide est choisi parmi les alkylène- et les polyalkylèneglycols. le glycérol, le xylitol. l'érythritol et le sorbitol, de préférence parmi le polyéthylèneglycol ou le polypropylèneglycol présent de sorte que le nombre de moles d'oxyde d'éthylène ou d'oxyde de propylène présents par mole de saccharide est compris entre 1 et 100.

7. Une méthode de réduction du besoin en eau d'une composition à base de ciment par addition d'un adjuvant selon l'une quelconque des revendications précédentes.

8. Une composition à base de ciment qui comprend un adjuvant selon l'une quelconque des revendications 1 à 6.